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⁸⁷Rb NMR LINESHAPE STUDY OF THE INCOMMENSURATE PHASE IN Rb₂ZnBr₄

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On going from the paraelectric (P) to the incommensurate (I) phase the ⁸⁷Rb 1/2 → 1/2 NMR lines in Rb₂ZnBr₄ broaden into a continuum which is limited by two edge singularities. The observed line shape and its temperature dependence are well described by the frequency distribution function predicted by the "plane wave" modulation model of the I phase. The anomalous temperature dependence of *T*₁ shows the presence of the phason branch in the I phase.

IT IS WELL KNOWN [1–3] that Rb₂ZnBr₄ becomes incommensurate below *T*_I = 82°C. The high temperature paraelectric (P) phase is orthorhombic and belongs to the space group *Pcmn*(*D*_{2h}¹⁶) with *a* = 13.343 Å, *b* = 7.656 Å, *c* = 9.708 Å and *z* = 4. The incommensurate (I) phase is characterized by a frozen in displacement wave with a wave vector *q*_δ = (1 – δ)*c*^{*}/3 which is an irrational fraction of the underlying lattice. The translational periodicity which is lost [4] in the I phase is restored (δ = 0) below *T*_c = –80°C where a "lock in"

transition to a commensurate (C) ferroelectric phase takes place with a tripling of the unit cell along the *c*-axis

In order to study the nature and the dynamics of the I phase we decided to perform a ⁸⁷Rb (*I* = 3/2) quadrupole perturbed NMR study of a single crystal of Rb₂ZnBr₄. The ⁸⁷Rb NMR spectra and spin–lattice relaxation times *T*₁ were measured at *ν*_L = 88.3 MHz using a superconducting magnet and a Fourier transform NMR spectrometer.

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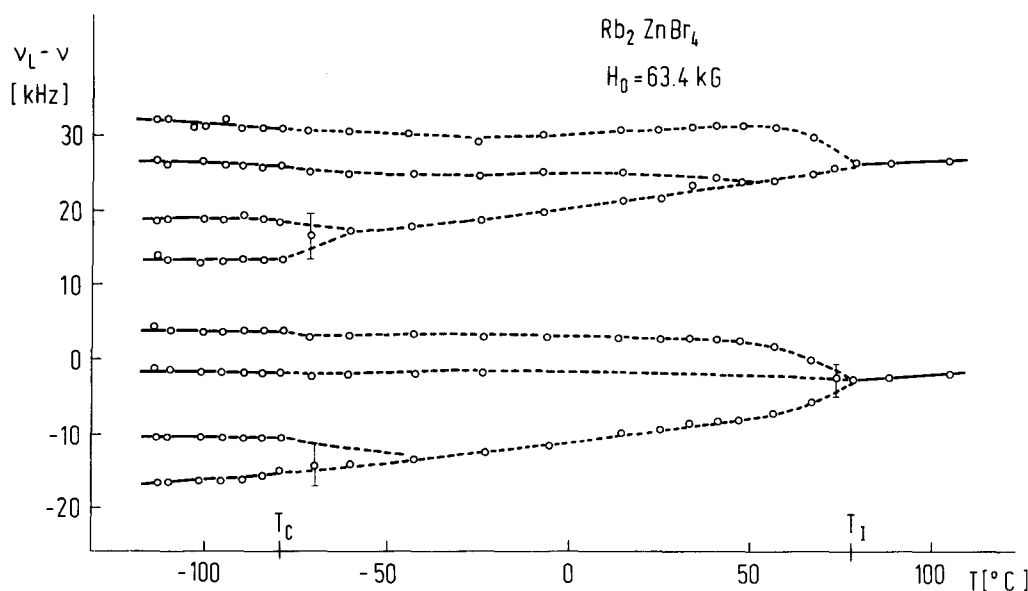


Fig. 1. Temperature dependence of the second order quadrupole shifts of the ⁸⁷Rb 1/2 → – 1/2 NMR lines in Rb₂ZnBr₄ at 88.3 MHz.

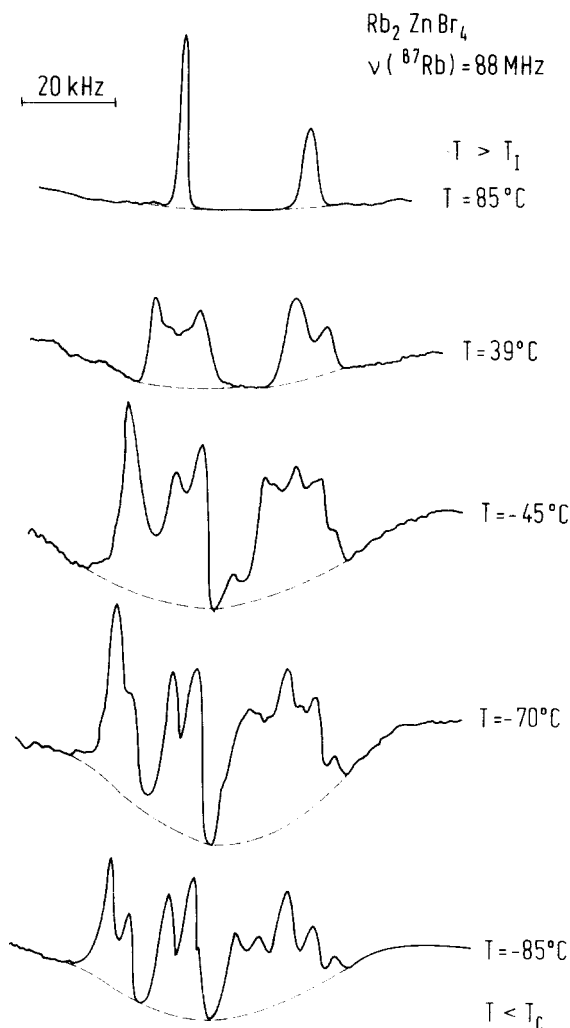


Fig. 2. ⁸⁷Rb NMR line shapes in the incommensurate phase of Rb₂ZnBr₄.

order quadrupole shifts of the central $1/2 \rightarrow -1/2$ ⁸⁷Rb NMR lines is shown in Fig. 1 for $\chi_c, H_0 = 45^\circ$. The two paraelectric lines — corresponding to the two chemically non-equivalent [5] ⁸⁷Rb sites in the high temperature unit cell, split and broaden at T_I but can be followed through the whole I phase into the C phase. The change in the line shape on going into the I phase is illustrated in Fig. 2. Close to T_I each paraelectric line broadens into a continuum which is limited by two edge singularities. The frequency separation between the two edge singularities increases on cooling below T_I . An additional structure appears at lower temperatures which changes only little on going into the C phase.

The observed NMR line shape in the I phase (Fig. 2) reflects the distribution of the electric field gradients (EFG) due to the incommensurability of the order parameter (i.e. the frozen in displacement wave) with the underlying crystal lattice. Expanding the EFG tensors at the Rb sites in powers of the lattice displacements

$$u(z) = A_0 \cos(q_\delta z + \phi) \quad (1)$$

we can express the second order quadrupole shift of a given ⁸⁷Rb $1/2 \rightarrow -1/2$ transition as

$$\Delta\nu_i \approx \Delta\nu_{i0} + \Delta\nu_{i1} \cos(q_\delta z_i + \phi) + \Delta\nu_{i2} \cos^2(q_\delta z_i + \phi) \dots \quad (2)$$

provided that the wavelength of the modulation, q_δ^{-1} , is large compared to the radius of the region where the dominant contribution to the EFG tensor comes from. Here $\Delta\nu_{i0}$ is the second order quadrupole shift in the P phase, $\Delta\nu_{i1}$ is proportional to the order parameter A_0 and $\Delta\nu_{i2}$ to A_0^2 . In the general case the linear term ($\Delta\nu_{i1}$) in the above expansion will be larger than higher order terms. If, however, the site symmetry of the Rb nucleus is high enough and if the orientation of the magnetic field is such that this symmetry is not destroyed, the linear term may be zero or small. In the C phase below T_c $\cos(q_\delta z_i + \phi)$ takes on a discrete value depending on the position of the investigated nucleus in the unit cell. In the I phase, on the other hand, the whole crystal is a unit cell and $\cos(q_\delta z_i + \phi)$ takes on nearly continuously all the values between +1 and -1 as z_i runs over all equivalent ⁸⁷Rb lattice sites. Reducing the phases $\varphi = q_\delta z_i + \phi$ to the interval $(0, 2\pi)$, one can introduce the density $\rho(\varphi)$, which is constant in this interval and zero outside. The frequency distribution $f(\nu)$ of the second order shifts due to incommensurate lattice displacements is thus obtained from

$$f(\nu) d\nu = \rho(\varphi) d\varphi \quad (3)$$

as [6]

$$f(\nu) = 1/(2\pi|d\nu/d\varphi|). \quad (4)$$

Here the distribution has been already normalized to unity, $\int f(\nu) d\nu = 1$.

In the “plane wave limit [7]” the incommensurate ordering is dominated by a single Fourier component of the displacement field and $\phi = \text{const}$. If terms linear in the order parameter are dominant ($\Delta\nu_1 \propto \sqrt{T - T_I}$, $\Delta\nu_2 \approx 0$), the frequency distribution will be given by:

$$f(\nu) = [2\pi\Delta\nu_1(1 - x^2)^{1/2}]^{-1} \quad (5a)$$

where $x = (\Delta\nu - \Delta\nu_0)/\Delta\nu_1$. The singularities corresponding to $x = \pm 1$ will occur at $\Delta\nu = \Delta\nu_0 + \Delta\nu_1$ and $\Delta\nu_0 - \Delta\nu_1$ where $d\nu/d\varphi = 0$. If, however, the site symmetry and the orientation of the crystal in the magnetic field is such that $\Delta\nu_1 = 0$ and the quadratic term dominates we find

$$f(\nu) = [4\pi\Delta\nu_2(1 - y^2)^{1/2}y]^{-1} \quad (5b)$$

with $y = [(\Delta\nu - \Delta\nu_0)/\Delta\nu_2]^{1/2}$. The frequency separation between the two singularities at $y = 0$ and $y = 1$ (i.e. the line width) will now be smaller than before as normally

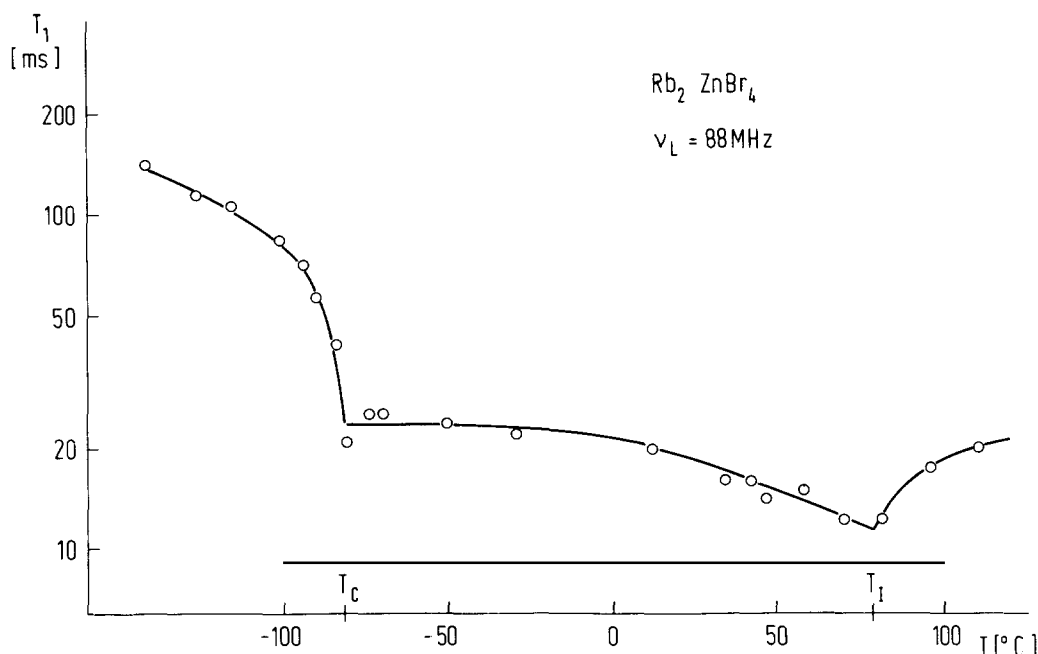


Fig. 3. Temperature dependence of the ^{87}Rb spin-lattice relaxation time in Rb_2ZnBr_4 .

$\Delta\nu_2 < \Delta\nu_1$. The position of the singularity at $y = 0$ (i.e. $\Delta\nu = \Delta\nu_0$) will not depend on temperature, whereas the position of the singularity at $\Delta\nu = \Delta\nu_0 + \Delta\nu_2$ will shift proportionally to $T - T_1$. The extension of the above analysis to the case where both linear and quadratic terms are present, is trivial. The positions of the two singularities will be in this case given by

$$\Delta\nu = \Delta\nu_0 + \Delta\nu_1 + \Delta\nu_2, \quad (6a)$$

and

$$\Delta\nu = \Delta\nu_0 - \Delta\nu_1 + \Delta\nu_2. \quad (6b)$$

If $|\Delta\nu_1| \leq 2|\Delta\nu_2|$, a third singularity appears at

$$\Delta\nu = \Delta\nu_0 - (\Delta\nu_1)^2 / (4\Delta\nu_2). \quad (6c)$$

In the “soliton limit” [7, 8] the incommensurate phase is best described as consisting of a series of regions of nearly commensurate ordering separated by domain walls (or phase solitons) at which the phase, $\phi = \phi(z)$, changes by $2\pi/3$. In such a case one would expect to see in the I phase sharp “commensurate” lines superimposed on a broad background originating from the incommensurate domain walls. The sharp “commensurate” domain lines would be practically unchanged at the “lock-in” transition $T = T_c$, where the broad domain wall lines vanish.

The observed ^{87}Rb line shapes in Rb_2ZnBr_4 (Fig. 2) are well described by the frequency distribution function (5a–b) predicted by the “plane wave limit” over the whole I phase except perhaps very close to T_c . The above results demonstrate that the “plane wave

limit” represents a good first approximation to the true situation in a large part of the I phase and that solitons may be important only at the low T end of this phase.

The conclusion that the plane wave approximation is a relatively good description of the I phase in Rb_2ZnBr_4 is as well supported by the ^{87}Rb spin-lattice relaxation data.

On approaching T_1 from above, T_1 — as measured on the $1/2 \rightarrow -1/2$ lines — exhibits a typical soft mode behaviour (Fig. 3) with T_1 decreasing as $T \rightarrow T_1^+$. This is analogous to what is observed in other structural phase transitions. In the I phase, on the other hand, the behaviour of T_1 is highly anomalous. Instead of increasing with increasing $T_1 - T$ the spin-lattice relaxation time T_1 is anomalously short and nearly independent of temperature in the whole I phase from $+82^\circ\text{C}$ to -80°C . On going through T_c , T_1 sharply increases by an order of magnitude and exhibits the usual soft mode behaviour in the C phase. The anomalously strong, nearly temperature independent mechanism which dominates T_1 in the I phase and which disappears on going to the C phase can be most easily explained as being due to the phason branch of the order parameter excitation spectrum.

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